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PREPARATION AND PROPERTIES OF MOLYBDENUM AND TUNGSTEN DINITROGEN COMPLEXES

XVI *. ELECTROCHEMICAL PROPERTIES OF TUNGSTEN AND MOLYBDENUM DIAZOALKANE COMPLEXES

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Summary

Diazoalkane complexes of type $[MF(NN{=}CRR')(dpe)_2][BF_4]$ (M = Mo or W; dpe = $Ph_2PCH_2CH_2PPh_2$), which are easily derived from bis(dinitrogen) complexes $[M(N_2)_2(dpe)_2]$, undergo consecutive one- and two-electron oxidations and reductions under voltammetric conditions at a platinum electrode. The ESR spectra of the species generated by the controlled potential electrolysis show that primary oxidation occurred on the metal atom (M = Mo) and reduction on the two nitrogen atoms in the diazoalkane ligands (M = Mo or W).

We have previously reported the preparation of diazoalkane complexes of type $[MF(NN{=}CRR')(dpe)_2][BF_4]$ from bis(dinitrogen) complexes, $[M(N_2)_2(dpe)_2]$ (M = Mo or W; dpe = $Ph_2PCH_2CH_2PPh_2$), as shown in eq. 1 [2,3]. This route consists of two steps: the protonation of one of the coordinating dinitrogen ligands to a hydrazido(2—) ligand, NNH_2, and the condensation of the hydrazido(2—) ligand with aldehydes and ketones. This reaction may be applied to bis(dinitrogen) complexes containing mono(tertiary) phosphine ligands, e.g., $[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W), where $[MX_2(NN{=}CRR')(PMe_2Ph)_3]$ (X = Cl or Br) are obtained [4,5]. This method is one of the most convenient routes for forming carbon—nitrogen bonds from coordinated dinitrogen, and thus the diazoalkane complexes are important intermediates in the conversion of coordin-

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* For part XV see ref. 1.

ated dinitrogen into organonitrogen compounds. We report here the results of studies of the electrochemical oxidation and reduction of these diazoalkane complexes of molybdenum and tungsten.

$$[M(N_2)_2(dpe)_2] \xrightarrow{HBF_4} [MF(NNH_2)(dpe)_2][BF_4]$$

$$\xrightarrow{RR'C=O} [MF(NN=CRR')(dpe)_2][BF_4] \qquad (1)$$

Results and discussion

Cyclic-voltammetric studies have shown that aryldiazomethane complexes of type $[MF(NN=CHC_6H_4X\text{-}p)(dpe)_2][BF_4]$ undergo reversible one-electron oxidation and reduction at a stationary platinum electrode in acetonitrile/0.1 *M* $[n\text{-}Bu_4N][BF_4]$. Further irreversible oxidation and reduction also were observed in almost all complexes except for four cases. Typical cyclic voltammograms are shown in Fig. 1 and 2 and the parameters are summarized in Tables 1 and 2. The oxidation and reduction of these complexes proceed in steps as shown in Scheme 1. The reduction of the *p*-nitrophenyldiazomethane complex of tungsten gave two reversible waves, the first of which is believed to

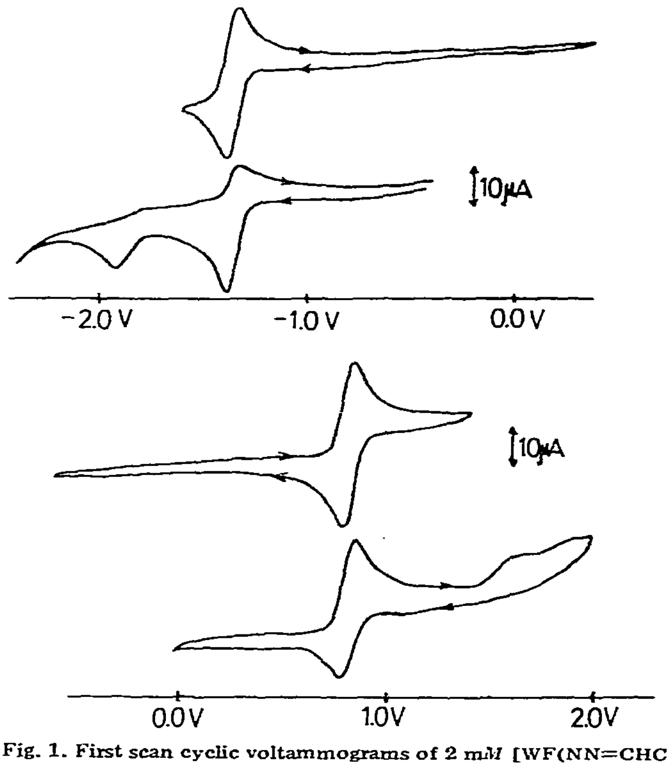


Fig. 1. First scan cyclic voltammograms of 2 m*M* $[WF(NN=CHC_6H_5)(dpe)_2][BF_4]$ in 0.1 *M* $[n\text{-}Bu_4N][BF_4]/CH_3CN$ at a platinum electrode with a scan rate 0.04 V/sec. Upper: one-electron and one- and two-electron reduction wave; lower: one-electron and one- and two-electron oxidation wave.

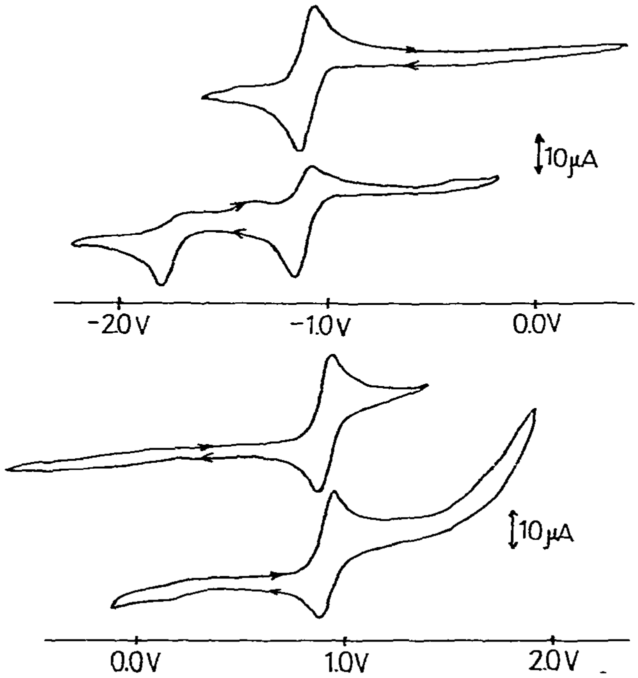


Fig. 2. First scan cyclic voltammograms of 2 mM [MoF(NN=CHC$_6$H$_5$)(dpe)$_2$][BF$_4$] in 0.1 M [n-Bu$_4$N]-[BF$_4$]/CH$_3$CN at a platinum electrode with s scan rate 0.04 V/sec. Upper: one-electron and one- and two-electron reduction wave; lower: one-electron oxidation wave.

TABLE 1

PARAMETERS OF ELECTROCHEMICAL OXIDATION OF DIAZOALKANE COMPLEXES

Complex [a]	E_{p1}^{ox}(V) [b]	$\lvert\Delta E_{p1}\rvert$(mV) [c]	$\left\lvert \frac{i_p^{ox}}{i_p^{red}} \right\rvert$	E_{p2}^{ox}(V) [b, e]
[WF(NN=CHC$_6$H$_4$NO$_2$)(dpe)$_2$][BF$_4$]	0.89	60	1.0	2.00
[WF(NN=CHC$_6$H$_4$Cl)(dpe)$_2$][BF$_4$]	0.81	60	1.1	1.60
[WF(NN=CHC$_6$H$_5$)(dpe)$_2$][BF$_4$]	0.83	70	1.1	1.60
[WF(NN=CHC$_6$H$_4$CH$_3$)(dpe)$_2$][BF$_4$]	0.84	60	1.0	1.60
[WF(NN=CHC$_6$H$_4$OCH$_3$)(dpe)$_2$][BF$_4$]	0.83	60	1.0	1.56
[WF{NN=CHC$_6$H$_4$N(CH$_3$)$_2$}(dpe)$_2$][BF$_4$]	0.67	60	1.0	1.09
[MoF(NN=CHC$_6$H$_4$Cl)(dpe)$_2$][BF$_4$]	0.97	60	0.95	n.o. [d]
[MoF(NN=CHC$_6$H$_5$)(dpe)$_2$][BF$_4$]	0.93	60	1.2	n.o. [d]
[MoF(NN=CHC$_6$H$_4$OCH$_3$)(dpe)$_2$][BF$_4$]	0.85	60	1.1	1.50
[WF(NN=CH$_2$)(dpe)$_2$][BF$_4$]	0.85	70	1.2	1.62
[WF(NN=CHCH$_2$CH$_3$)(dpe)$_2$][BF$_4$]	0.79	60	1.0	1.52
[WF{NN=C(CH$_3$)CH$_2$COCH$_3$}(dpe)$_2$][BF$_4$]	0.79	60	0.84	1.32
[WBr$_2${NN=C(CH$_3$)C$_6$H$_4$Cl}(PMe$_2$Ph)$_3$]	0.04	60	0.94	1.16
[WBr$_2${NN=C(CH$_3$)C$_6$H$_5$}(PMe$_2$Ph)$_3$]	0.07	70	0.99	1.18
[WBr$_2${NN=C(CH$_3$)C$_6$H$_4$OCH$_3$}(PMe$_2$Ph)$_3$]	0.03	50	1.0	1.11

[a] All substituents of aryl groups are in *para*-position. [b] Peak oxidation potential vs. s.c.e. at a scan rate 0.04 V/sec. [c] $|\Delta E_{p1}| = |E_{p1}^{ox} - E_{p1}^{red}|$. [d] n.o. = not observed. [e] Irreversible processes except for those commented otherwise.

TABLE 2

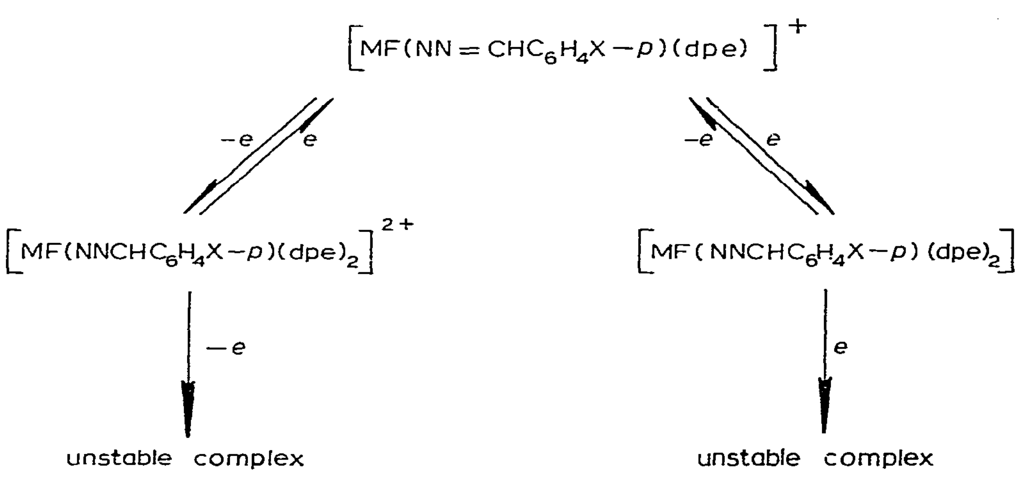
PARAMETERS OF ELECTROCHEMICAL REDUCTION OF DIAZOALKANE COMPLEXES

Complex [a]	E_{p1}^{red}(V) [b]	$\lvert\Delta E_{p1}\rvert$(mV) [c]	$\left\lvert\frac{i_{p1}^{red}}{i_{p1}^{ox}}\right\rvert$	E_{p2}^{red}(V) [b,]
$[WF(NN{=}CHC_6H_4NO_2)(dpe)_2][BF_4]$	−0.77	60	1.0	−1.02 [f]
$[WF(NN{=}CHC_6H_4Cl)(dpe)_2][BF_4]$	−1.34	60	0.82	−1.85
$[WF(NN{=}CHC_6H_5)(dpe)_2][BF_4]$	−1.39	60	1.0	−1.93
$[WF(NN{=}CHC_6H_4CH_3)(dpe)_2][BF_4]$	−1.45	50	1.0	−1.99
$[WF(NN{=}CHC_6H_4OCH_3)(dpe)_2][BF_4]$	−1.48	60	1.0	−2.10
$[WF\{NN{=}CHC_6H_4N(CH_3)_2\}(dpe)_2][BF_4]$	−1.60	60	1.0	−2.11
$[MoF(NN{=}CHC_6H_4Cl)(dpe)_2][BF_4]$	−1.07	60	1.1	−1.72
$[MoF(NN{=}CHC_6H_5)(dpe)_2][BF_4]$	−1.16	60	1.1	−1.81
$[MoF(NN{=}CHC_6H_4OCH_3)(dpe)_2][BF_4]$	−1.30	70	1.0	n.o. [d]
$[WF(NN{=}CH_2)(dpe)_2][BF_4]$	−1.45	—	—	−2.12
$[WF(NN{=}CHCH_2CH_3)(dpe)_2][BF_4]$	−1.75	—	—	n.o. [d]
$[WF\{NN{=}C(CH_3)CH_2COCH_3\}(dpe)_2][BF_4]$	−1.82	—	—	n.o. [d]
$[WBr_2\{NN{=}C(CH_3)C_6H_4Cl\}(PMe_2Ph)_3]$	−1.56	—	—	−2.16
$[WBr_2\{NN{=}C(CH_3)C_6H_5\}(PMe_2Ph)_3]$	−1.61	—	—	−1.92
$[WBr_2\{NN{=}C(CH_3)C_6H_4OCH_3\}(PMe_2Ph)_3]$	−1.44	70	1.0	−1.68

[a] All substituents of aryl groups are in *para*-position. [b] Peak reduction potential vs. s.c.e. at a scan rate 0.04 V/sec. [c] $\lvert\Delta E_{p1}\rvert = \lvert E_{p1}^{red} - E_{p1}^{ox}\rvert$. [d] n.o. = not observed. [e] Irreversible processes except for those commented otherwise. [f] Reversible process with $\lvert\Delta E_{p2}\rvert$ = 60 mV and $\lvert i_p^{red}/i_p^{ox}\rvert$ = 0.95.

be due to the reduction of *p*-nitrophenyl group. The secondary oxidation of phenyldiazomethane and *p*-chlorophenyldiazomethane complexes of molybdenum and the secondary reduction of the *p*-methoxyphenyldiazomethane complex of molybdenum were not detected. The reversible one-electron oxidation of the *p*-dimethylaminophenyldiazomethane complex probably occurred on the *p*-dimethylaminophenyl group.

SCHEME 1



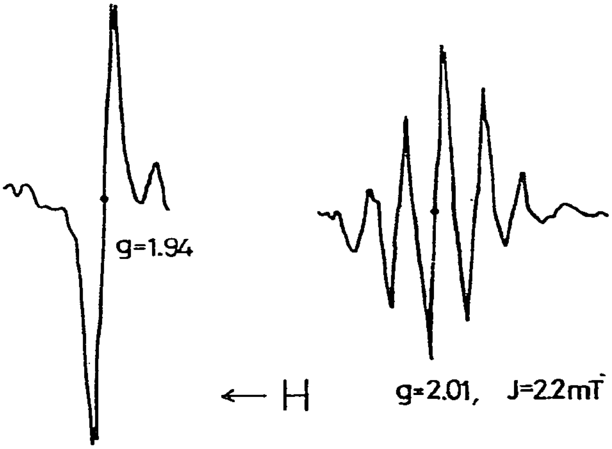


Fig. 3. ESR spectra obtained during the electrolysis of the complex $[MoF(NN{=}CHC_6H_5)(dpe)_2][BF_4]$ in CH_2Cl_2. Left: oxidation; right: reduction.

The ESR spectra of the paramagnetic species generated in situ by the controlled potential electrolysis of the complex $[MoF(NN{=}CHC_6H_5)(dpe)_2][BF_4]$ in 0.1 *M* $[n\text{-}Bu_4N][BF_4]/CH_2Cl_2$ at room temperature are shown in Fig. 3. The singlet signal at $g = 1.94$, which appeared during the electrolysis at the potential corresponding to the primary oxidation, is explained by the localization of the unpaired electron on the molybdenum atom. On the other hand, the paramagnetic species formed by electro-reduction at the primary reduction potential gave a quintet resonance with 1/2/3/2/1 intensity ratio at $g = 2.01$, which indicates that the unpaired electron is delocalized over the two nitrogen atoms of the diazoalkane ligand. The hyperfine structure observed is ascribed to the coupling to the two ^{14}N nuclei ($I = 1$) with $\langle A_N \rangle = 2.2$ mT. This result distinctly shows that the highest occupied molecular orbital (HOMO) of this complex corresponds to the orbital located in the molybdenum atom and the lowest unoccupied molecular orbital (LUMO) of this complex to that extending to the two nitrogen atoms. In the case of the tungsten analogue $[WF(NN{=}CHC_6H_5)(dpe)_2][BF_4]$, a quintet resonance appears at $g = 2.00$ with $\langle A_N \rangle = 2.6$ mT by the electro-reduction, which is essentially the same result as that observed for the molybdenum analogue. However, the unpaired electron corresponding to the one-electron oxidation could not be detected.

Fig. 4 shows the correlation of the primary oxidation and reduction potentials with Hammett σ constants. Good linear relationships are observed between the σ values and reduction potentials in both the molybdenum and tungsten complexes with the gentler slope of V/σ value for tungsten than for molybdenum, where the more electron-donating the substituent the more negative is the reduction potential. Also, when comparing the molybdenum and the tungsten complexes with the same substituent, the tungsten complex shows more negative reduction potentials than the molybdenum analogue, which indicates that the LUMO of the tungsten complex is higher than that of the molybdenum analogue. A similar relationship between σ values and oxidation potentials of the molybdenum complexes also is observed, but in the case of tungsten the

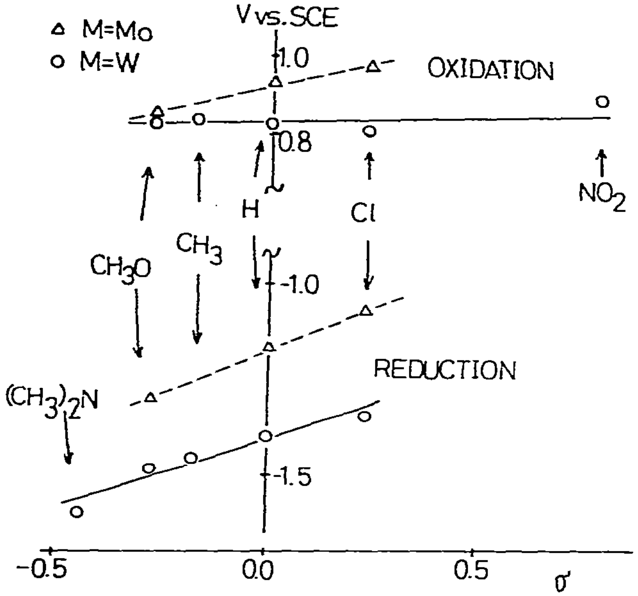
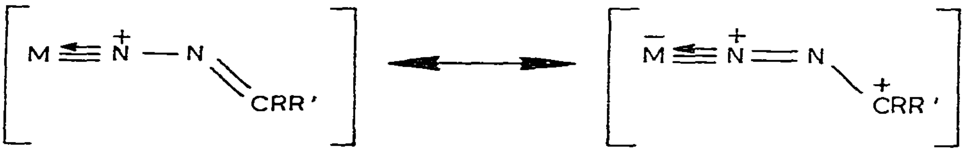


Fig. 4. Correlation of oxidation and reduction potentials for the diazoalkane complexes [$MF(NN{=}CHC_6H_4X\text{-}p)(dpe)_2][BF_4]$ with Hammett σ constants.

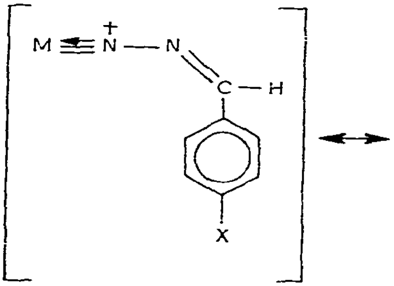
oxidation potentials apparently are independent of the substituents. Since the ESR spectra of the molybdenum complexes show that one electron oxidation occurs on the molybdenum atom, this result shows that the electronic effect of the terminal substituent extends to the molybdenum atom via the conjugated system. Chatt and his coworkers have previously studied the electro-oxidation of the aryldiazenido complexes [$Mo(N_2C_6H_4X)(S_2CNMe_2)_3$], and they also observed a linear correlation between the one-electron oxidation potentials and the σ values of X, but with a larger gradient of V/σ value than the one shown in Fig. 4. They concluded that there is restricted resonance stabilisation of the cation species by delocalisation of the charge from the aromatic ring into the diazenido nitrogens and that the influence of the substituent X is essentially inductive [6].

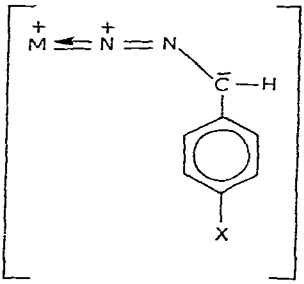
As reported in a previous paper [3], X-ray structural analysis of [$WF\{NN{=}C(CH_3)CH_2COCH_3\}(dpe)_2$][$BF_4$]. THF has shown that the W—N—N linkage is essentially linear. The angle N—N—C is 125.2(19)° and the bond orders of the C—N and N—N bonds are about 1.7 and 1.4, respectively. On the other hand, Chatt and his coworkers had found that the nitrogen-bearing carbon in [$WBr(NN{=}CH_2)(dpe)_2$]Br is susceptible to nucleophilic attack by hydride ion or methyl carbanion [7]. Thus, we described the diazoalkane ligand as a combina-

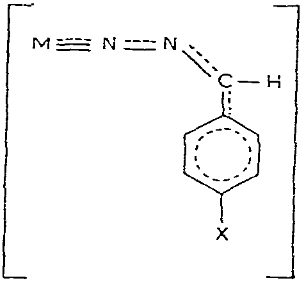


(i) (ii)

tion of the two resonance structures (i) and (ii) [3]. However, at least in the case of aryldiazomethane complexes of tungsten, the diazoalkane ligand may be understood best by the two resonance structures (iii) and (iv). The latter is generated by electron flow from the metal to the nitrogen-bearing carbon, since the more electron-withdrawing is the substituent X, the lower is the C=N stretching frequency; that is, the larger is the contribution of the structure (iv) (Table 3). Thus, the electronic effect of the substituent X transmitted to the nitrogen atoms in the diazoalkane ligand and the central metal is described by structure (v), and this effect appears as the linear correlation of the Hammett σ constants with the oxidation potentials (M = Mo) and the reduction potentials (M = Mo or W).


(iii)

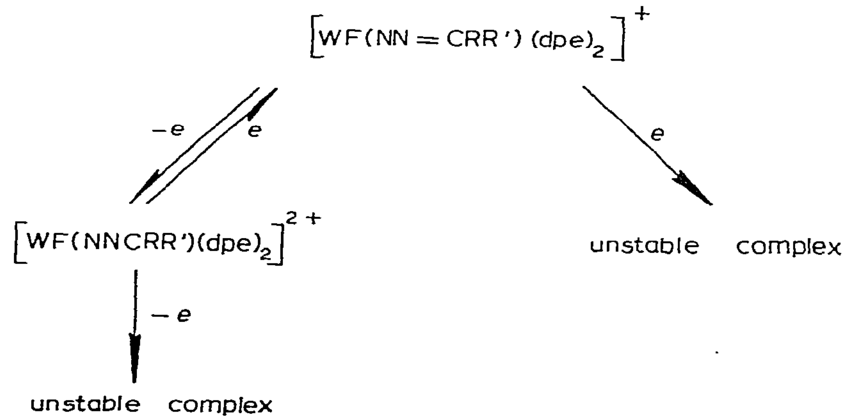

(iV)


(V)

Cyclic voltammograms of the alkyldiazomethane complexes of tungsten show that reversible one-electron oxidation occurs, followed by secondary irreversible oxidation, and one or two irreversible reduction waves appear. These processes are summarized in Scheme 2. The aryl group is considered to make some contribution to the stabilization of the one-electron reduced species.

Cyclic voltammograms of the neutral diazoalkane complexes of tungsten, $[WBr_2\{NN{=}C(CH_3)C_6H_4X\text{-}p\}(PMe_2Ph)_3]$, also are recorded. Reversible one-electron oxidation is observed at 0.04, 0.07 or 0.03 V, followed by irreversible

SCHEME 2



(R = R' = H; R = Et, R' = H ; R = CH_3 , R' = CH_2COCH_3)

TABLE 3

THE C=N STRETCHING FREQUENCIES OF THE COMPLEXES $[WF(NN{=}CHC_6H_4X\text{-}p)(dpe)_2][BF_4]$ [a]

X	NO_2	Cl	H	CH_3	OCH_3	$N(CH_3)_2$
ν(C=N) (cm^{-1})	1510	1532	1536	1531	1534	1555

[a] KBr disks on a Hitachi 215 spectrometer.

two-electron oxidation, when X = Cl, H or OCH_3, respectively (Table 1). These one-electron oxidation potentials apparently are independent of the σ values of the substituents, which is the same result as that observed for the complexes $[WF(NNCHC_6H_4X\text{-}p)(dpe)_2][BF_4]$. The low oxidation potentials of $[WBr_2\{NN{=}C(CH_3)C_6H_4X\text{-}p\}(PMe_2Ph)_3]$, compared to those of $[WF(NN{=}CRR')(dpe)_2]^+$ (R, R' = alkyl or aryl), is due to the neutrality of the diazoalkane complexes of PMe_2Ph. In comparison with the oxidation potential of the hydrazido(2—) complex $[WBr_2(NNH_2)(PMe_2Ph)_3]$ measured by Chatt and his coworkers at —0.060 V [8], we have come to the conclusion that the energy of the HOMO of the diazoalkane complex is lower than that of the hydrizido(2—) complex.

We are now trying to isolate the species generated by the electrochemical oxidation and reduction for the better understanding of these redox processes.

Experimental

All experimental procedures were carried out under a dry nitrogen atmosphere. Solvents were rigorously dried by the usual methods and distilled under a nitrogen atmosphere before use. Aldehydes, ketones and tetra-n-butylammonium tetrafluoroborate were commercially obtained and used without further purification.

Preparation of diazoalkane complexes

The green diazoalkane complexes, $[MF(NN{=}CRR')(dpe)_2][BF_4]$ (M = Mo or W), were prepared in a similar manner as already reported [3]. As a typical example, the preparation of $[WF(NN{=}CHC_6H_5)(dpe)_2][BF_4]$ is described below. The red diazoalkane complexes $[WBr_2\{NN{=}C(CH_3)C_6H_4X\text{-}p\}(PMe_2Ph)_3]$ (X = Cl, H or OCH_3) were prepared according to the published method [4,5].

Preparation of $[WF(NN{=}CHC_6H_5)(dpe)_2][BF_4]$

To a stirred suspension of $[W(N_2)_2(dpe)_2]$ (1.00 g, 0.964 mmol) in 20 ml of THF was added dropwise a 42% aqueous HBF_4 solution (0.5 ml). After stirring for 3 h at room temperature, the yellow-orange solution obtained was evaporated in vacuo nearly to dryness. To the sticky residue were added CH_2Cl_2 (6 ml) and benzaldehyde (0.78 ml, 0.77 mmol) and this mixture was stirred for 8 h at a room temperature to give a green solution. This was concentrated in vacuo to about half volume and filtered. Slow addition of hexane to the filtrate gave the title complex as a green crystalline solid, which was washed with ether and hexane and then dried in vacuo (1.11 g, 95%).

Other diazoalkane complexes of type $[MF(NN{=}CRR')(dpe)_2][BF_4]$ were prepared analogously in 65—95% yield. New diazoalkane complexes were identified by the analytical and/or spectroscopic data.

$[WF(NN{=}CHC_6H_4NO_2)(dpe)_2][BF_4] \cdot \frac{1}{2}CH_2Cl_2$. Anal. Found: C, 55.42; H, 4.23; N, 3.28. Calcd.: C, 55.30; H, 4.22; N, 3.25%. ν(C=N): 1510 cm^{-1}. δ(NN=C*H*): 5.9 ppm.

$[WF(NN{=}CHC_6H_4Cl)(dpe)_2][BF_4]$. Anal.: Found: C, 57.27; H, 4.38; N, 2.18. Calcd.: C, 57.41; H, 4.59; N, 2.20%. ν(C=N): 1532 cm^{-1}. δ(NN=C*H*): 5.9 ppm.

$[WF(NN{=}CHC_6H_4CH_3)(dpe)_2][BF_4] \cdot \frac{1}{2}CH_2Cl_2$. Anal.: Found: C, 57.66; H, 4.42; N, 2.32. Calcd.: C, 57.61; H, 4.56; N, 2.22%. ν(C=N): 1531 cm^{-1}. δ(NN=C*H*): 5.7; $\delta(C_6H_4CH_3)$: 2.3 ppm.

$[WF(NN{=}CHC_6H_4OCH_3)(dpe)_2][BF_4]$. Anal.: Found: C, 57.39; H, 4.48; N, 2.24. Calcd.: C, 58.36; H, 4.58; N, 2.27%. ν(C=N): 1534 cm^{-1}. δ(NN=C*H*): 5.7; $\delta(C_6H_4OCH_3)$: 3.9 ppm.

$[WF\{NN{=}CHC_6H_4N(CH_3)_2\}(dpe)_2][BF_4]$. ν(C=N): 1555 cm^{-1}. δ(NN=C*H*): 5.7; $\delta(N(CH_3)_2)$: 3.1 ppm.

$[MoF(NN{=}CHC_6H_4OCH_3)(dpe)_2][BF_4]$. Anal.: Found: C, 62.47; H, 5.11; N, 2.41. Calcd.: C, 62.84; H, 4.93; N, 2.44%. ν(C=N): 1530 cm^{-1}.

$[MoF(NN{=}CHC_6H_4Cl)(dpe)_2][BF_4]$. ν(C=N): 1535 cm^{-1}.

$[WBr_2\{NN{=}C(CH_3)C_6H_4OCH_3\}(PMe_2Ph)_3]$. ν(C=N): 1520, 1530(sh) cm^{-1}.

$[WBr_2\{NN{=}C(CH_3)C_6H_4Cl\}(PMe_2Ph)_3]$. ν(C=N): 1530, 1520(sh) cm^{-1}.

Electrochemical methods

All electrochemical experiments were carried out in H-type cells, where both compartments were separated from each other by a grade 3 glass frit. The working electrode was a platinum wire approximately 0.055 cm^2 in area in voltammetric experiments while a platinum wire about 1.24 cm^2 in area was used in preparative experiments. The auxiliary electrode was a large platinum plate. Throughout the present study, the potentials were referred to s.c.e., separated from the working electrode by a salt bridge filled with base electrolyte to avoid the water contamination. Tetra-n-butylammonium tetrafluoroborate was used as supporting electrolyte.

ESR recording of paramagnetic species

The ESR spectra of the paramagnetic species formed by the oxidation or reduction of the complexes $[MF(NN{=}CHC_6H_5)(dpe)_2][BF_4]$ (M = Mo or W) at a platinum electrode in the quartz ESR tube were recorded on a JEOL 3BS-X spectrometer. Typical concentrations used in ESR studies were 2 mmol/l solution in 0.1 mol/l $[n\text{-}Bu_4N][BF_4]CH_2Cl_2$.

References

1 K. Iwanami, Y. Mizobe, T. Takahashi, T. Kodama, Y. Uchida, and M. Hidai, Inorg. Chem., submitted.
2 M. Hidai, Y. Mizobe, and Y. Uchida, J. Amer. Chem. Soc., 98 (1976) 7824.
3 M. Hidai, Y. Mizobe, M. Sato, T. Kodama, and Y. Uchida, J. Amer. Chem. Soc., 100 (1978) 5740.
4 P.C. Bevan, J. Chatt, M. Hidai, and G.J. Leigh, J. Organometal. Chem., 160 (1978) 165.
5 Y. Mizobe, Y. Uchida, and M. Hidai, Bull. Chem. Soc. Japan, 53 (1980) 1781.
6 G. Butler, J. Chatt, G.J. Leigh, and C.J. Pickett, J. Chem. Soc. Dalton, (1979) 113.
7 R. Ben-Shoshan, J. Chatt, W. Hussain, and G.J. Leigh, J. Organometal. Chem., 112 (1976) C9.
8 J. Chatt, A.J. Pearman, and R.L. Richards, J. Chem. Soc., Dalton, (1978) 1766.